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# Anoxic Corrosion of Low-Carbon Steel at Elevated Temperatures—Effects of Chloride and Sulfide



PRESENTED BY

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## 2 History of Anoxic Corrosion at Waste Isolation Pilot Plant

### US DOE Waste Isolation Pilot Plant (WIPP)

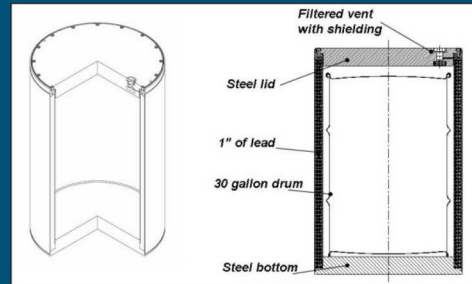
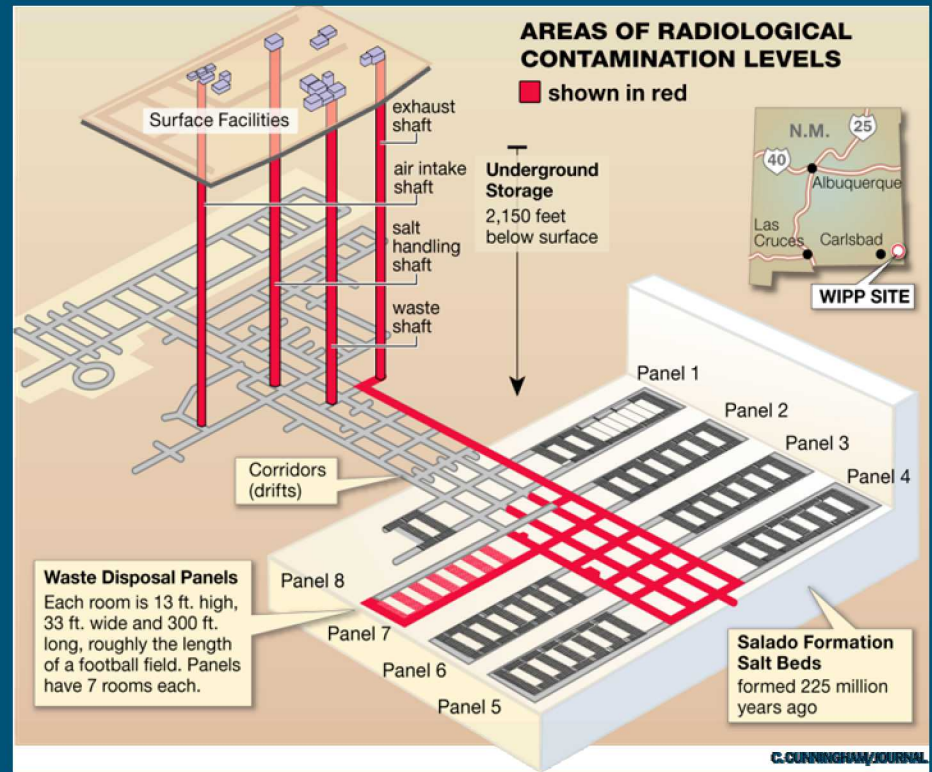
- Nation's only deep geological repository for nuclear waste

### Sandia National Laboratories

- Scientific and technical advisor to the DOE

### Iron (Fe) in WIPP

- Waste itself
- Low Carbon Metal Containers used for waste emplacement
- $1.6 \times 10^7$  kg Iron metal waste



### Chloride and Sulfide in WIPP

- Chloride-sulfate Brines
- Halite
- $H_2S$  formed by microbial activity

\*Anoxic conditions expected approximately 100 yrs after WIPP closure.



Quantify the dissolution rate of the low-carbon steel (C1018) in the presence or absence of chlorides (NaCl and MgCl<sub>2</sub>) or sulfides (NaHS) at 90°C and pH(25°C) = 9.

- Single-Pass Flow-Through (SPFT) experiments.
- Static experiments (only solid characterization).
- Use of polished coupons (50 mm×50 mm× 6 mm).

Rates were determined by:

- Interferometry on coupons (novel application).
- Assay of total Fe by ICP-MS (still awaiting results)
- Release of H<sub>2</sub>(g) from steel coupon. (still awaiting results)
- Weight loss of coupons.



Experiments performed in a glove box ( $0.2 < O_2 < 0.4$  ppmv).

Temperature set to  $90^\circ C$ , solutions set to  $pH(25^\circ C) = 9.0$

Baseline solutions:

- Either Simplified Generic Weep Brine (SGWB), or
  - $3.5\text{ M NaCl} + 1\text{ M MgCl}_2$
- DI water

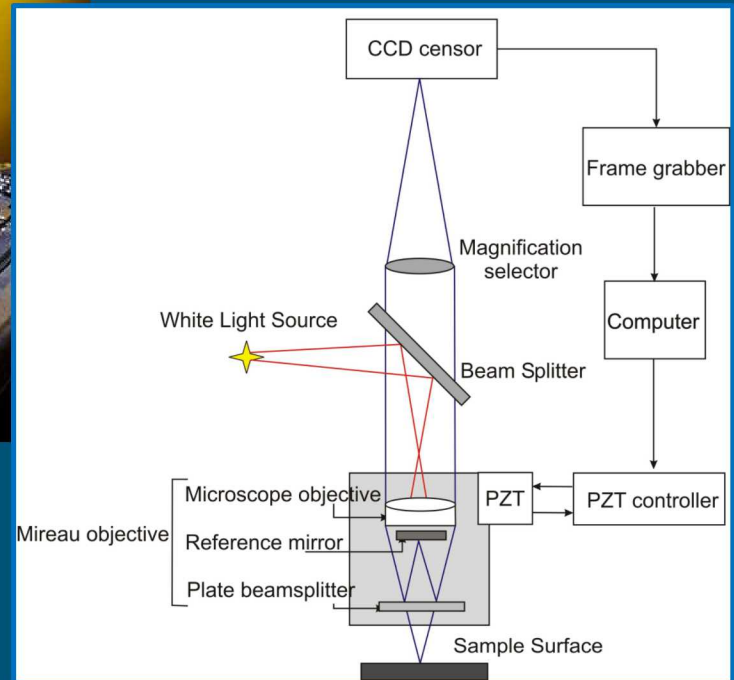
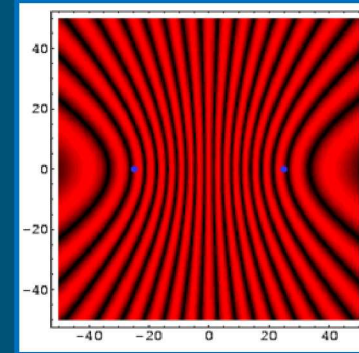
Subdivided into sulfide-free or sulfide-bearing:

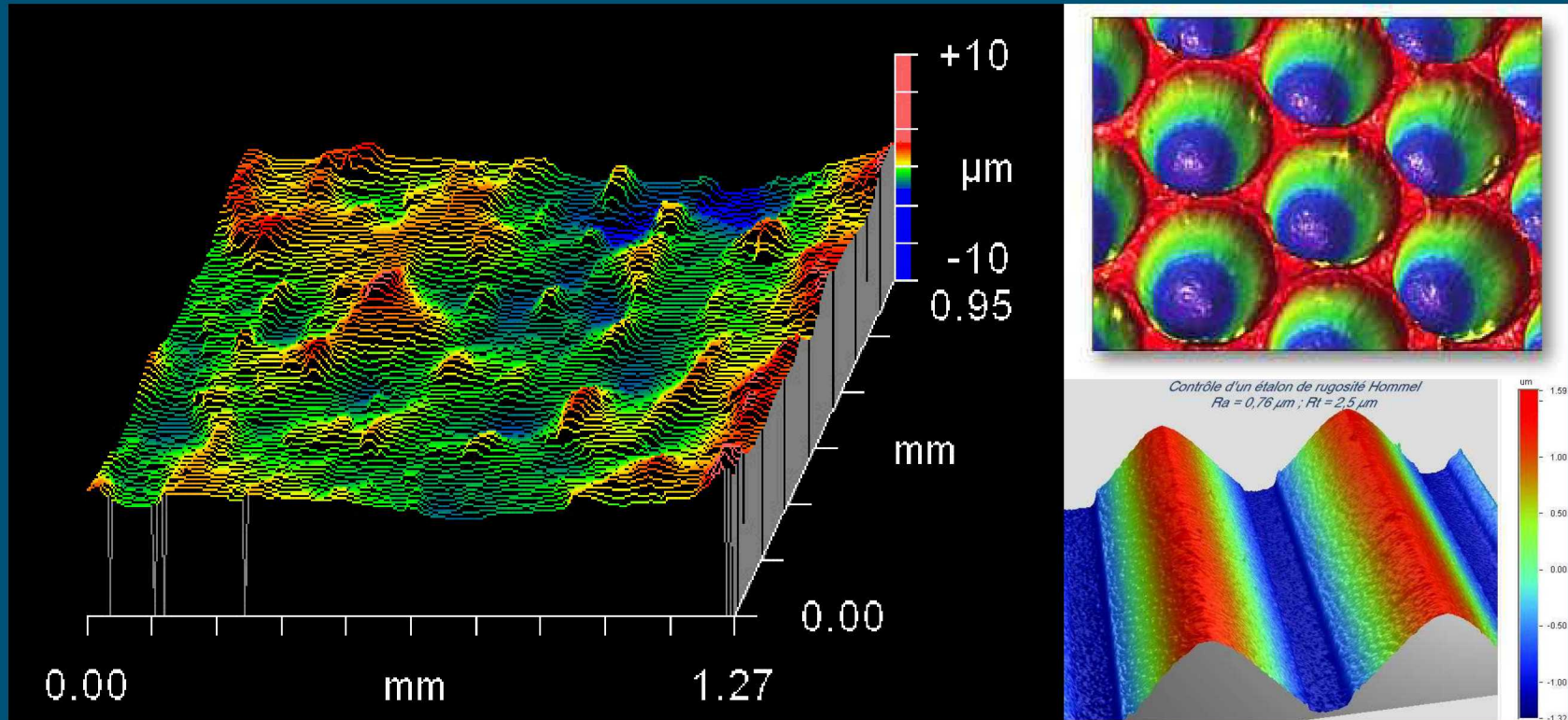
- Sulfide-bearing consisted of 1, 5 or 10 mmol NaHS

Flow-rate set to  $\sim 60$  mL/day (exchange of 1 reactor volume every other day).

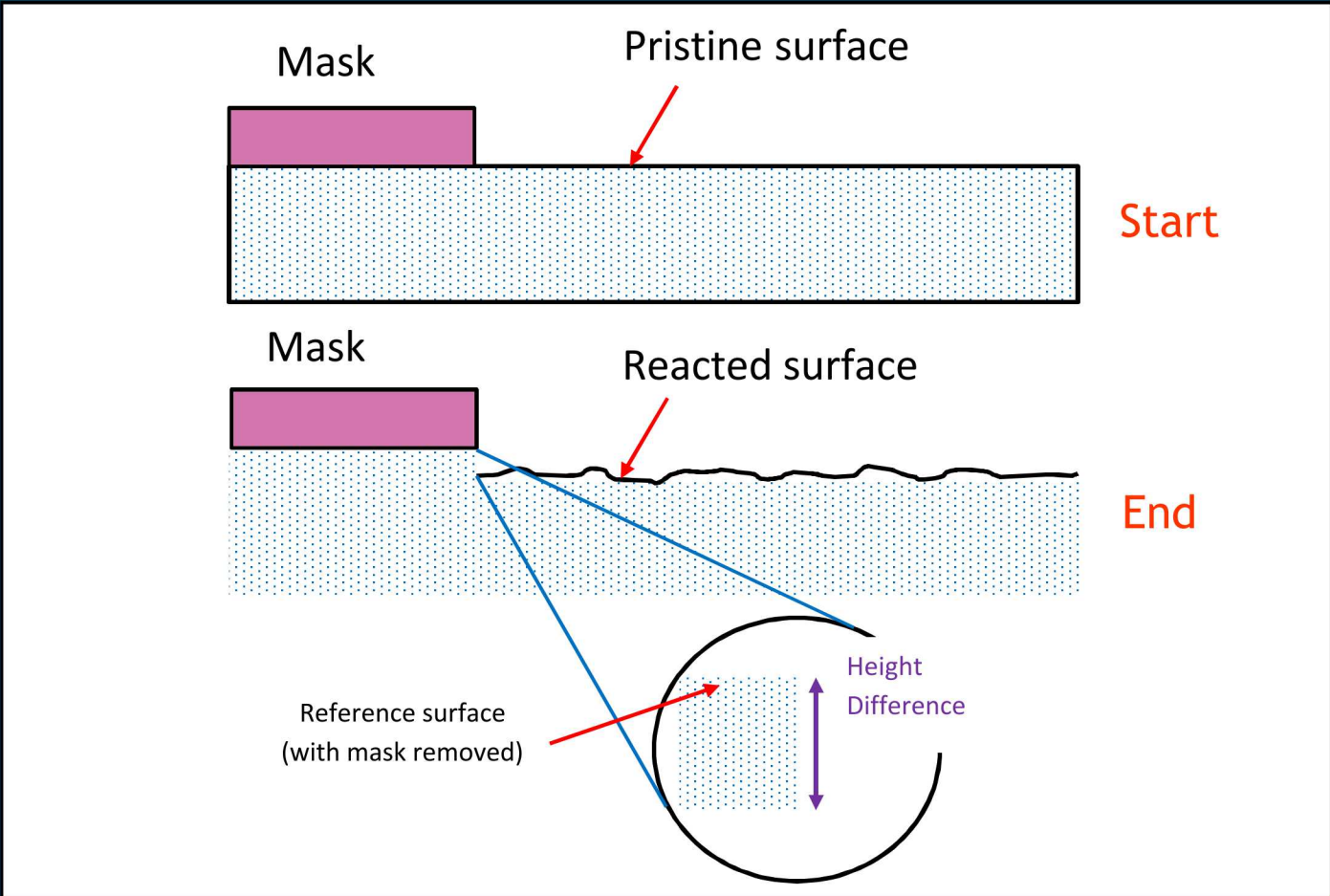
Ran for 5 months' duration at which point steady-state equilibrium achieved.

# 5 Interferometry Measurements





7 | Summary of interferometry strategy



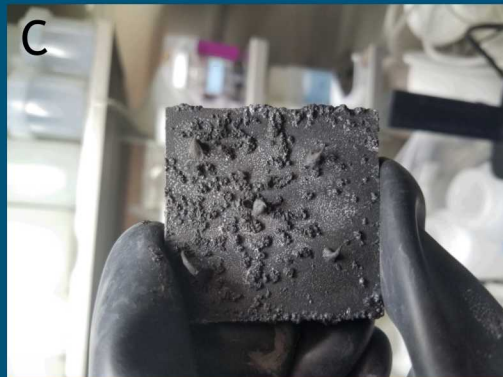
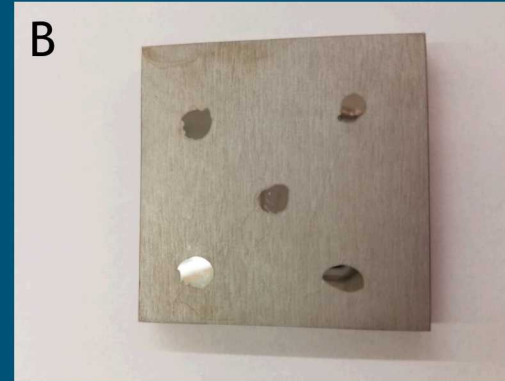
$$\text{Rate} = \rho \frac{\Delta h}{\Delta t}$$

$\rho$  is the steel coupon density

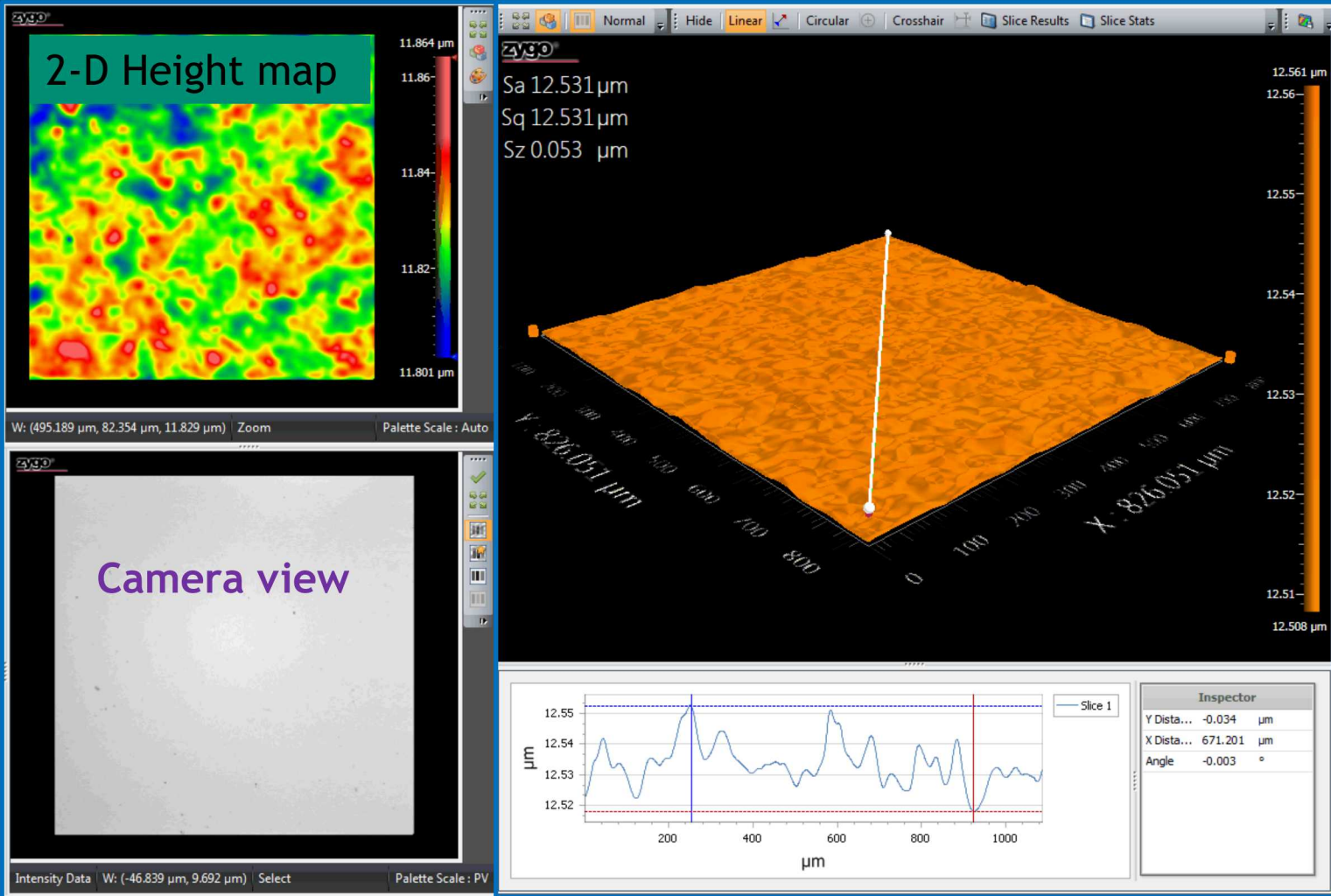
$\Delta h$  is the height difference between the reference and reaction surfaces

$\Delta t$  is elapsed time

- Cut and polish steel coupons.
- Measure coupon dimensions using electronic calipers.
- “Mask” a small portion of the coupon.
- Expose coupon to solution in flow-through reactor.
- Remove coupon from reactor, remove mask, measure the change in height between reference and reaction surface.



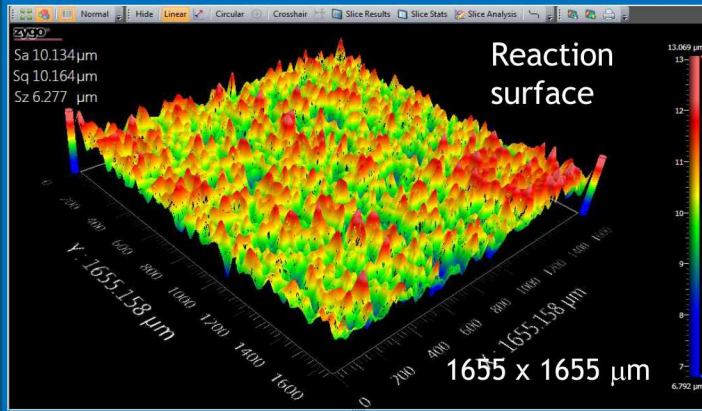
Photographs of post-experiment steel coupons. A. Coupon 113 (SGWB) before cleaning. B. Coupon 113 after cleaning. C. Coupon D (SGWB + NaHS) before cleaning. D. Coupon D after cleaning.



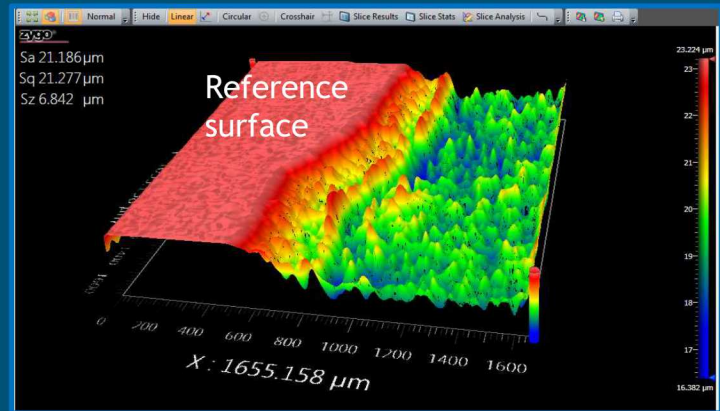
Small height differences across the surface (average of  $\sim 35\text{nm}$ )

# Simplified Generic Weep Brine (reacted)

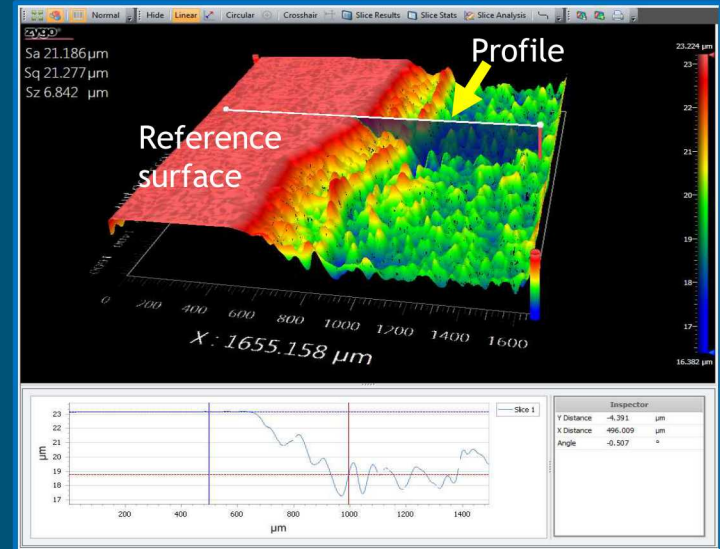
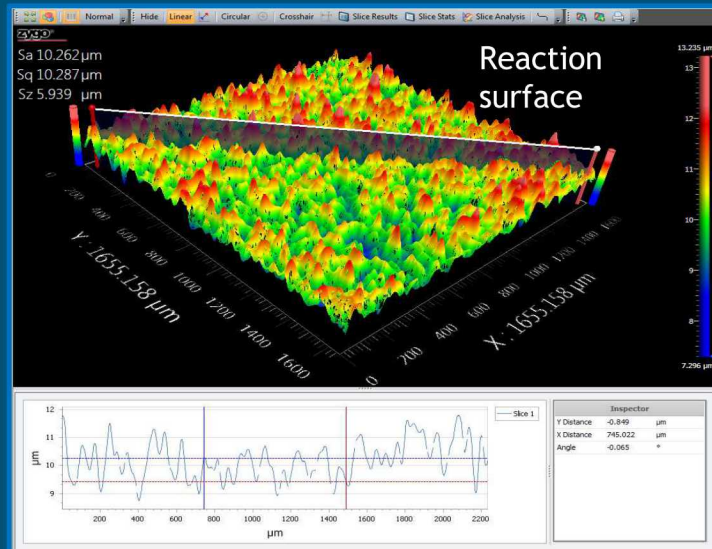
5 months, 60 mL/d flow-rate



Reaction surface showing an increase in surface roughness

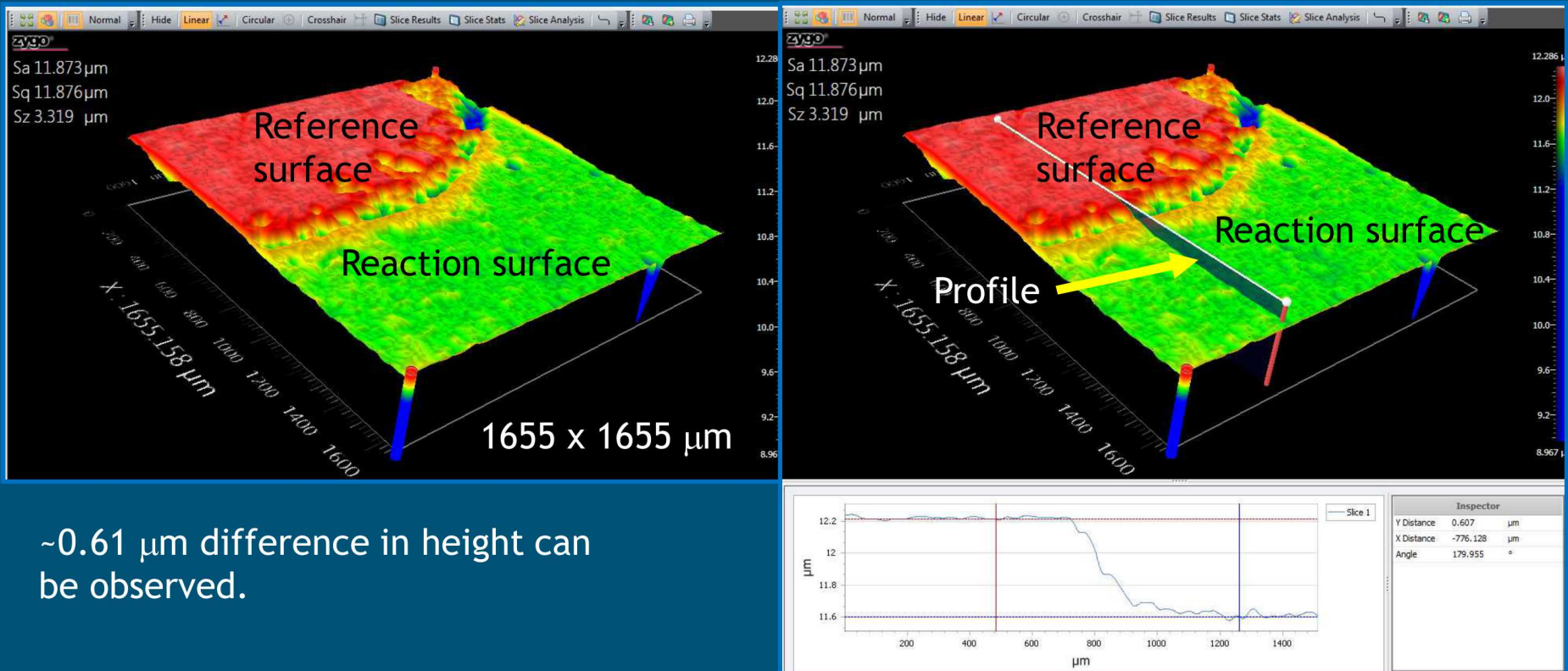


~4.4  $\mu\text{m}$  difference in height can be observed between Reaction and Reference surface

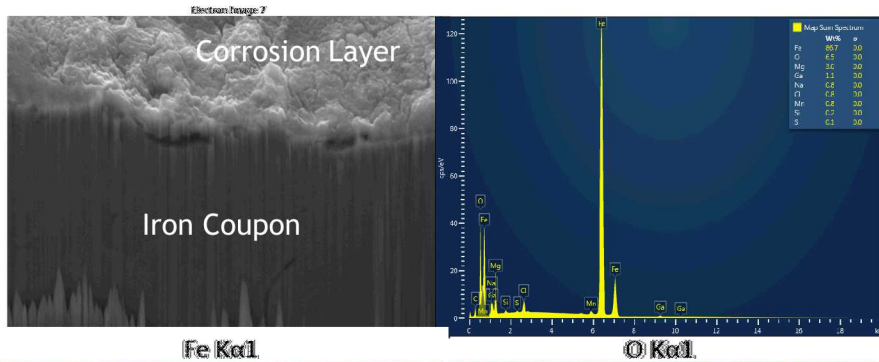


5 months, 60 mL/d flow-rate

Both reference and reaction surfaces displayed

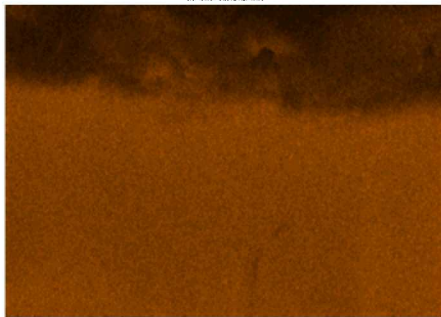


# Cross Sectional SEM & EDS images of iron coupon

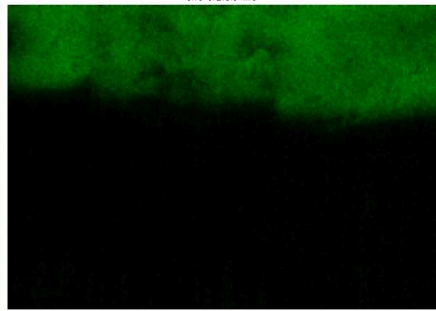


Fe Kα1

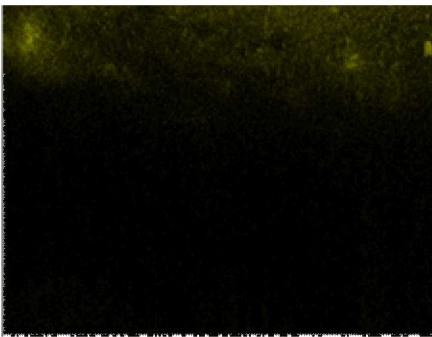
O Kα1



10µm



Mg Kα1\_2

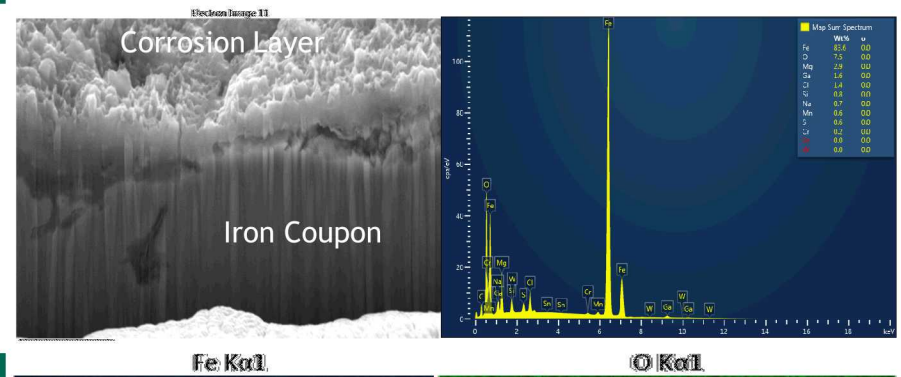


10µm



10µm

SGWB

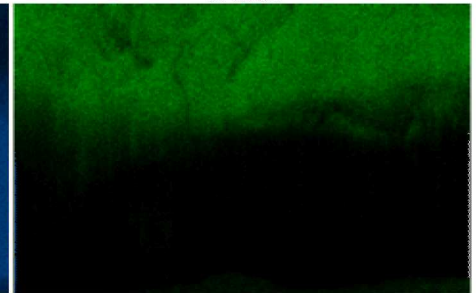


Fe Kα1

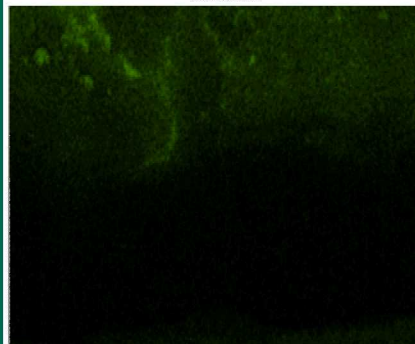
O Kα1



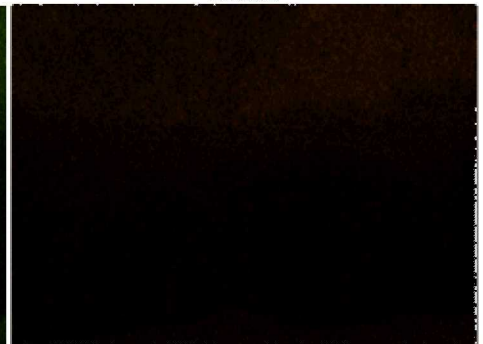
Cl Kα1



S Kα1

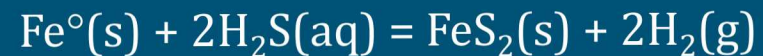
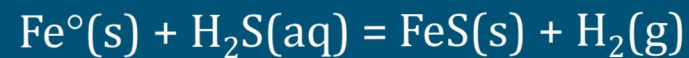
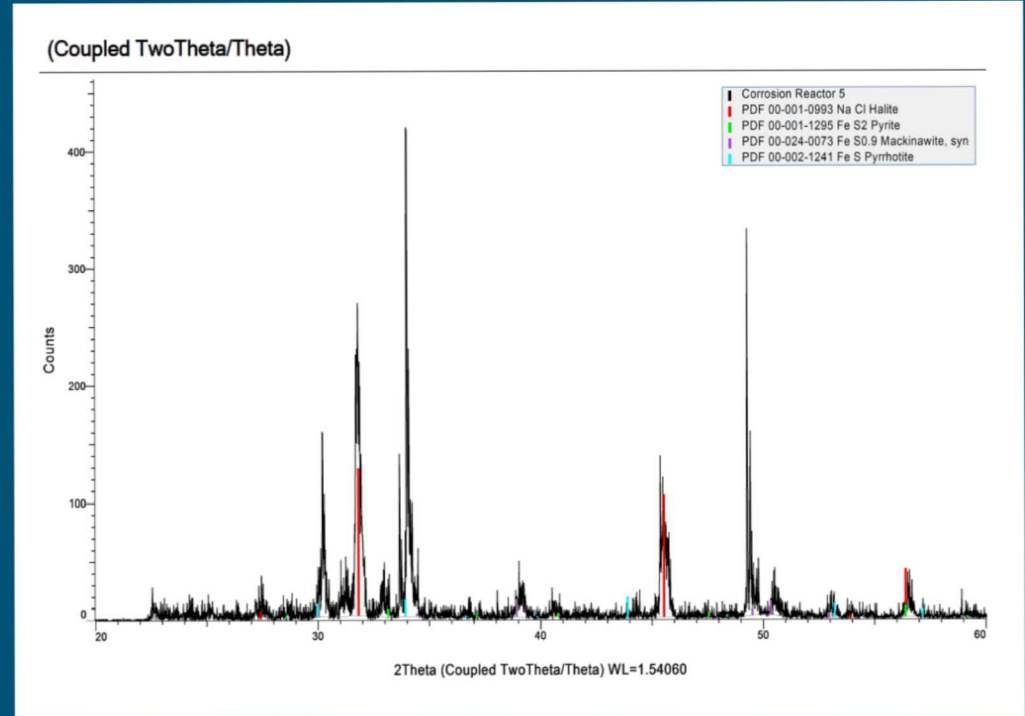
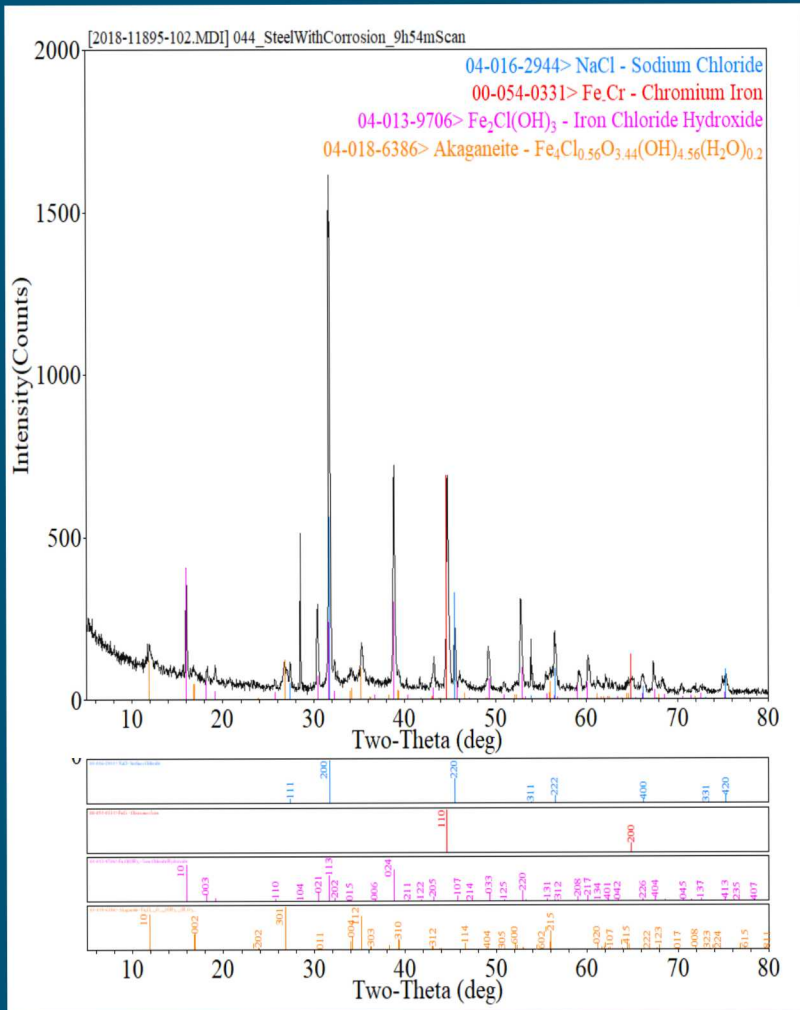


5µm



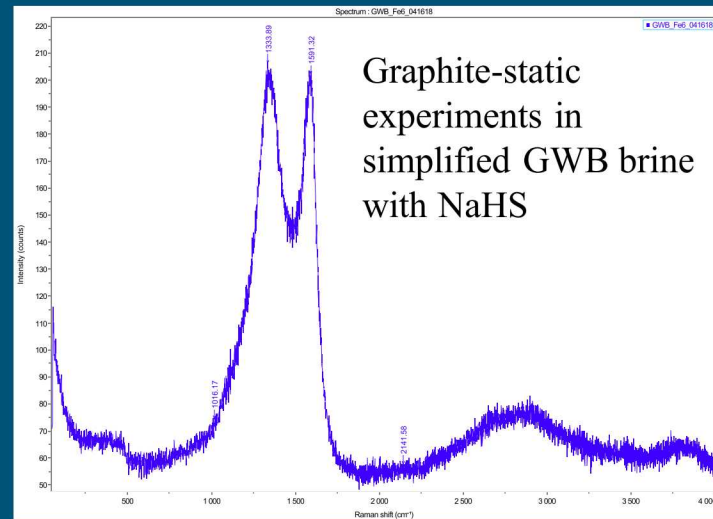
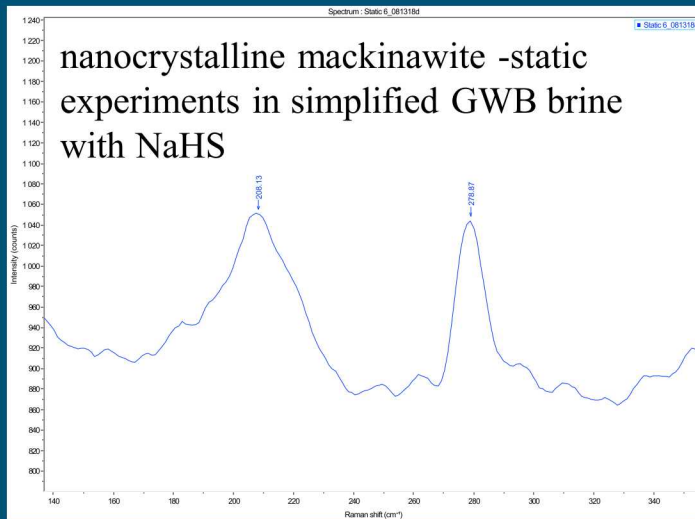
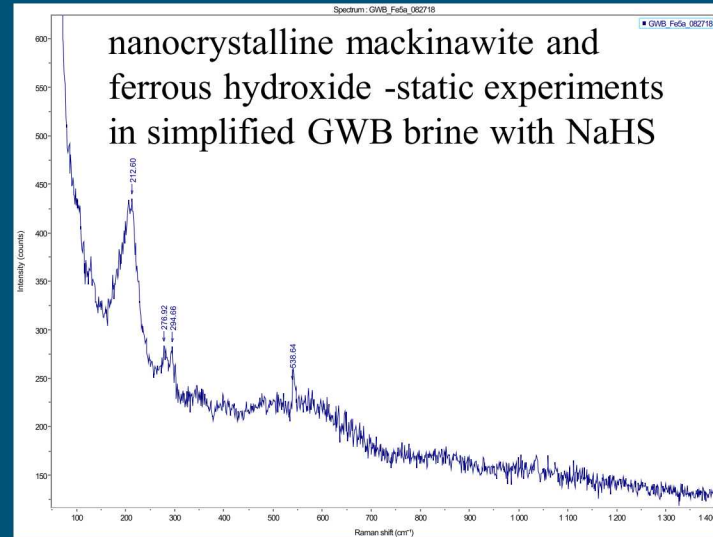
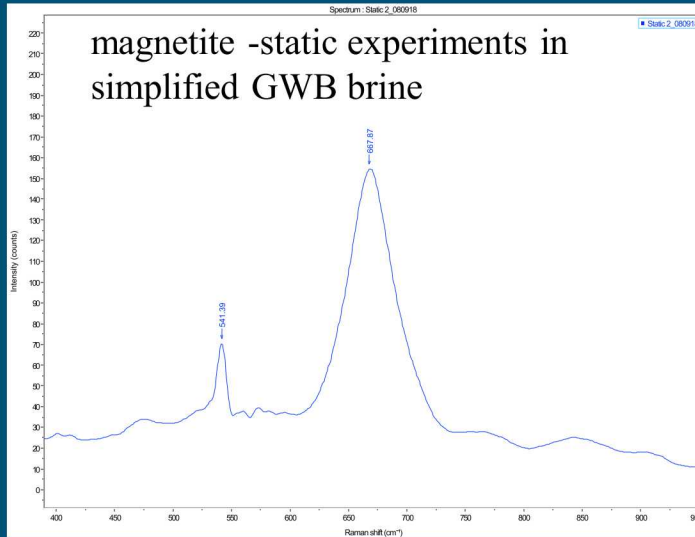
5µm

SGWB + NaHS



**Looking at Fe to H<sub>2</sub>(g) ratio**

# Characterization of Corrosion Products-Raman Spectroscopy



- Steel coupons experienced faster dissolution ( $\sim 12 \mu\text{m}/\text{yr}$ ) in SGWB solutions at  $90^\circ\text{C}$  and  $\text{pH}(25^\circ\text{C}) = 9.0$  in the absence of sulfide.
- Coupons reacted in SGWB + NaHS also showed dissolution, but at much slower rates due to passivation layer.
- Coupons reacted in DI water reacted at a much slower rate than SGWB solutions.
- These rates can be efficiently measured by interferometry.
- Interferometry, therefore, shows great promise in quantifying dissolution rates of steel.